Optical characterisation of RF sputter coated palladium thin films for hydrogen sensing

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ABSTRACT

We investigate the optical properties of Pd thin films of the thickness 20-100nm deposited on Si wafer via RF sputter coating. The Pd samples are characterised using white light interfermometry for thickness and ellipsometry for refractive index. We demonstrate the independence of refractive index on film thickness above 20nm. Considerable discrepancy is found between our measurement and previously published complex refractive indices for both bulk and RF sputter coated Pd, indicating a high degree of dependence on deposition technique.

Keywords: sensing, hydrogen, palladium, thin film

1. INTRODUCTION

Hydrogen is often cited as a viable portable fuel of the future[1, 2]. With a low ignition energy and an explosive range of 4-97%[3] in air, the very same properties making hydrogen a suitable fuel, also present dangers in storage and transportation. There is therefore a clear need for a fast, reliable and accurate hydrogen sensor for leak detection. Current hydrogen detectors are generally based on the catalytic activity of palladium[3]. Palladium absorbs large quantities of hydrogen, almost 900[4] times its own volume, and in doing so measurable reversible[5] changes occur to the properties of palladium due to straining of the crystal lattice [6] and decreased electron mobility.

Current electrical sensors rely on this change in resistivity due to changes in electron mobility [3, 7]. While fast and reasonably accurate, these sensors compound safety issues by bringing electrical current, needed for operation, and heating into the vicinity of an explosive gas. Therefore there has been considerable work of late into palladium based optical hydrogen detection. A large number of proposed designs have been presented[2, 4, 8, 9] but the creation of a fast, reliable and accurate sensor has been frustrated by a confused picture in the published optical constants of palladium, particularly the change in optical properties as it absorbs hydrogen[10-14].

As part of an ongoing study into the change in optical properties of thin film palladium as a function of hydrogen absorption we have characterised the optical properties of RF sputter coated thin film palladium in the absence of hydrogen to provide a reliable, precise baseline for future sensor development work.

2. EXPERIMENTAL SETUP

Due to finite hydrogen mobility within a Pd lattice homogeneous films of the order of 10-100nm in thickness are most useful for sensing applications, with thicker films demonstrating unacceptably long response times[15]. RF sputter coating is the coating technique of choice as the relatively low deposition energies, particularly compared to thermal evaporation; result in a flat homogenous layer of Pd[14]. Ellipsometry is a practical means to characterise films of this type. The process involves measuring the change in polarisation on reflection at a known angle of incidence. This is typically rendered into an amplitude ratio, Ψ, and the phase difference, ∇[16].

These two measureands can be used in conjunction with a model of the sample material to derive optical properties. In the case of our samples the model is a homogenous, flat film of unknown refractive index and optical thickness deposited onto an effectively infinite silicon substrate. It is only possible to return two optical properties, typically refractive index and optical thickness of a dielectric. As Pd is a metal film with a complex index, it is only possible to return the real and imaginary components of the index; the film thickness needs to be determined independently.

To that end we have used a process of short coherence interfermometry, or white light interfermometry (WLI), to determine film thickness using a Zygo NewView 5000. Our WLI technique is based on measuring a step change between coated and uncoated substrate. Pd films <80nm are partially transparent to white light and as such it is impractical to measure the step between coated and uncoated-substrate directly since reflection surfaces become ambiguous. Instead an optically thick, >100nm, layer of Al is deposited uniformly over the Pd coated substrate. Careful deposition preserves the Pd step function, providing an unambiguous reflection surface and identical optical properties either side of the step. It is, however, impossible to perform an ellipsometry measurement through this Al layer so it is necessary to create a complex sample structure with separate areas suitable for WLI and ellipsometry, Figure 1.

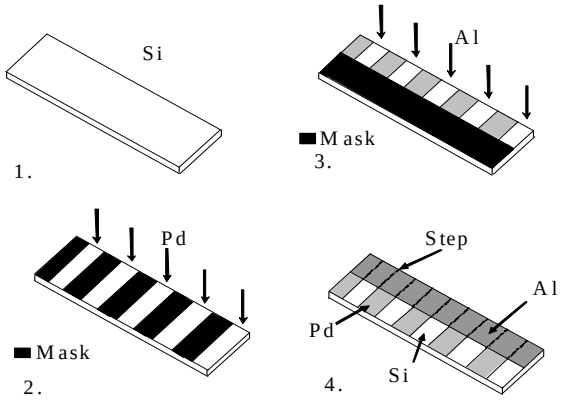

Figure 1: Illustration of sample preparation steps 1) substrate wafer, 2) deposition of Pd via RF sputter coating though a strip mask, 3) Overcoat deposition of Al via thermal evaporation through a mask, 4) completed sample with areas of Pd for ellipsometry and step functions in Al for WLI.

Samples were generated using a two step coating process, Figure 1, with an Edwards AUTO 306 Vacuum Coating chamber for thermal deposition with an additional AJA International A320 Magnetron Sputter Coating system for PF sputter deposition of Pd. An internal armature allows for both steps to be carried out without repressurisation. Pd was deposited via RF sputter coating at a plasma power of 70W with samples suspended 100mm above a 99.9% pure Pd target in $3x10^{-3}$mBar Ar. To provide the necessary strip step functions the sample is positioned 0.2mm behind a 0.1mm mask. The mask is fixed relative to the Pd target and all other parameters held constant such that only the coating time was varied between samples. Al was deposited via thermal evaporation to a thickness of ~100nm, monitored via a quartz crystal thickness monitor. Once the Al overcoat was applied the samples were left to cool in situ, under vacuum, for 10 minutes and then removed for characterised with WLI.

The WLI is calibrated via a reference step function. This reference step function is only provided with a certified height ±10nm. While the Zygo has an accuracy of at least ±1nm this error in calibration is expected to manifest its self as a systematic error in measured film thickness, although the measurement error is expected to be small.

Ellipsometry measurements were carried out with a Woollam M-2000 at AWE Aldermaston, with no more than 48hrs between sample preparation and measurement to prevent possible build up of oxides or surface contamination. The ellipsometer directly measured Ψ and ∇ between 200-900nm for each measurement site on each sample, Figure 1. These data were then analysed using the WVASE32 software package under various models, discussed in the next section, to return values for n, k and film thickness, d. In addition a separate sample of 100nm Pd was sent to J.A. Woollam inc. for independent verification of our measurement and to extend the spectral range to 1550nm although these data are not presented here.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2a shows a plot of measured Ψ and ∇ for a range of prepared samples. As the film thickness is expected to be directly proportional to the coating time this has been used to label samples. The plot clearly demonstrates a pattern indicating a proportionality of coating time to both Ψ and ∇. This is expected and can be attributed to a combination of change in film thickness with coating time and a contribution by the change in refractive index which in itself is expected to be dependent on film thickness especially for very thin samples.

In order to analyse the data it is necessary take each assumption in turn. By assuming that the proportionality of Ψ and ∇ to sample coating time shown in Figure 2a is due solely to a change in film thickness we may use previously published values for the refractive index of Pd[17] to recover the film thickness. Figure 2b shows a comparison of the film thickness retrieved by this assumption and that directly measured for the same samples by WLI. Of note is the generally good agreement between the two sets of data below a thickness of 40nm. At longer coating times, 120s ~40nm thickness, the deposited Pd film becomes opaque and ellipsometry is unable to derive an accurate film thickness resulting in a plateau at about 40nm.

Of greater interest is that the two measurement techniques maintain good agreement for thinner films. If the refractive index of the films were dependant on film thickness then we would expect the two datasets presented in Figure 2b to be divergent for thinner films. As this is not the case this suggests that the refractive index of the films is indeed independent of film thickness over the investigated range.

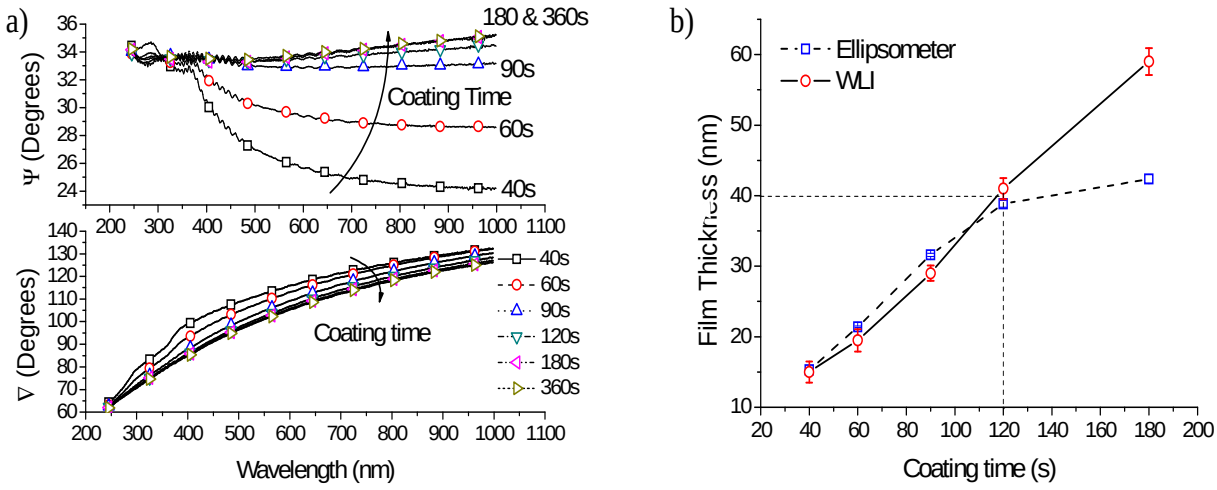

Figure 2: a) Measured Ψ (upper) and ∇ (lower) data for a series of Pd samples. b) Film thickness vs coating time measured by WLI and calculated via ellipsometry assuming bulk Pd refractive index.

The alternative hypothesis is to assume that the WLI measurements for film thickness are accurate and to attempt derive the complex refractive index of the films from the Ψ and ∇ data. These data can be seen in Figure 3a. Of interest here is the loss of clear proportionality between film thickness and complex index compared to the proportionality in Figure 2a. Again this suggests that there is little or no dependence between film thickness and refractive index in the investigated range.

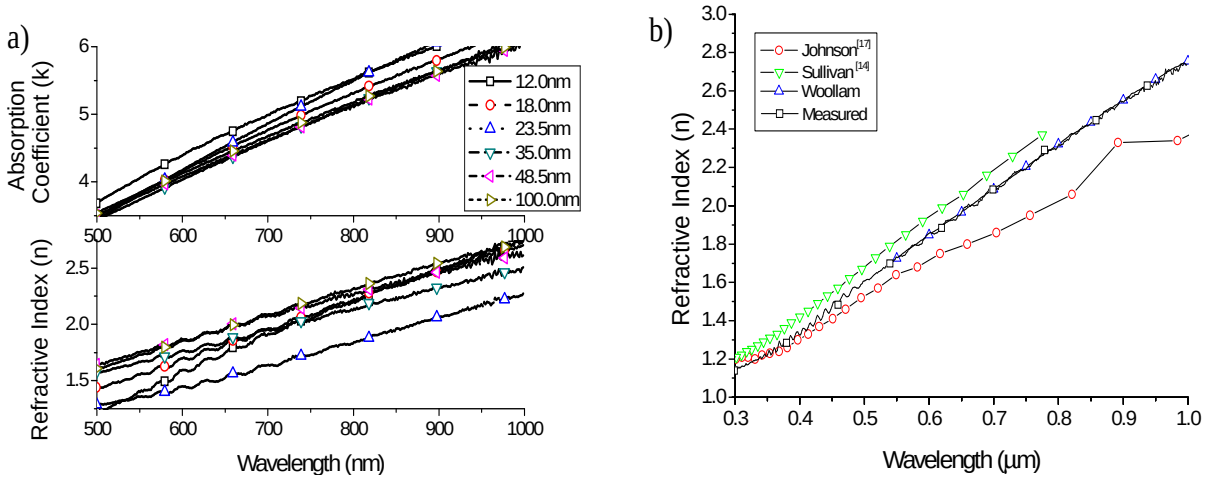

Figure 3: a) Plots of calculated complex refractive index based on fitting WLI measured film thickness to measured Ψ and ∇. b) Comparative plot of published refractive index for bulk like Pd from various sources.

4. CONCLUSIONS

The refractive index of these thin films is found to be independent of film thickness above ~20nm which compares favourably with previously published material[10, 18]. Figure 3b illustrates the difference between standard bulk Pd refractive index (Johnson[17]), previously published RF sputter coated Pd thin films (Sullivan[14]), our results for film thicknesses above 20nm and the sample sent to Woollham for independent measurement. While it is expected that the optical properties of thin films deposited by RF sputter coating will differ significantly from bulk material[14] the relatively poor agreement between our measurements and those taken by Sullivan is surprising particularly as there is such good agreement between our results and the independent measurement carried out by Woollam.

Both our samples and Sullivan's are deposited using similar systems and with comparable parameters. It has been shown that argon pressures above a threshold affect the resultant crystal structure through increased surface mobility[14]. Since we have generated our data at an Argon pressure an order of magnitude below this threshold it can be ruled out as a contributing factor for the disagreement seen in Figure 3b. A substrate - Pd lattice disparity can similarly be discounted as this would result in a proportionality with film thickness which only occurs for films below 20nm.

The poor agreement between these data cannot therefore be easily dismissed. It is clear that the optical properties of thin film Pd, while not dependant on film thickness above a threshold, are highly dependent on deposition parameters even between similar setups. It is therefore essential for Pd films to be optically characterised, rather than relying on published data, before adequate modelling and optimisation of Pd based sensors can take place.

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